Studies on the Determination of Arsenic. IX : Photometric Determination of Arsenic in Iron and Steel by Extraction with Organic Solvents

Studies on the Determination of Arsenic. IX
Photometric Determination of Arsenic in Iron and Steel by Extraction with Organic Solvents*

Hidehiro GOTÔ and Yachiyo KAKITA

The Research Institute for Iron, Steel and Other Metals

(Received March 9, 1955)

Synopsis

In the photometric determination of arsenic as to be molybdenum blue, phosphorus shows the same absorption as arsenic. Therefore, the determination of arsenic had to be studied after separation of arsenic from phosphorus. It was found that before the reduction to molybdenum blue, phosphorus in the form of molybdate alone was extracted with organic solvents, while arsenic salt was not extracted. Phosphorus molybdate was completely extracted with amyl alcohol in 0.1～0.4N of sulfuric acid. This procedure was applied to the photometric determination of arsenic in iron and steel, and satisfactory results were obtained.

I. Introduction

In the 2nd report of this series[1], the colorimetric determination of arsenic as to be molybdenum blue was described. This method, however, was found to be inconvenient because the co-existing phosphorus showed the coloration together with that of arsenic; so after phosphorus had been determined by another method and its value had been subtracted, or after arsenic was isolated preliminarily, the colorimetry had to be carried out. In order to remove such inconvenience, an attempt was made to determine arsenic alone by previously removing phosphorus. Extraction of phosphorus as a molybdate with an organic solvent before reduction to molybdenum blue has already been reported in the colorimetric determination of silicon[2],[3]. The application of this method for the determination of arsenic was carried out and it was found that only phosphorus was extracted but not arsenic; satisfactory results were obtained in the photometric determination of arsenic, which will be reported in the present paper.

II. Experimental results

1. Fundamental experiments

Molybdemun blue, from either arsenic or phosphorus, is extracted with organic solvents and the separations of both are impossible. Before reduction, however,

* The 799th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, **17** (1953), 450.

(1) Y. Kakita, Sci. Rep., RITU, **A1** (1949), 399.

(2) K. J. Jensen and C. J. Rodden, Natl. Nuclear Energy Ser., Div. VIII, 1, Anal. Chem., Manhattan Project, **218** (1950); Chem. Abstract, **45** (1951), 1914.

(3) Katô and Okinaka, read at the 12th Tôhoku Local Meeting of the Chemical Society of Japan, May 22, 1950.

in the form of a molybdate, that of phosphorus alone is extracted with organic solvents. There has been no report on arsenic, and so the following examination was carried out:

(i) Apparatus and reagents

Apparatus: Determination of absorbance was made by the Pulfrich's photometer with an incandescence lamp as the light source, S_{72} (729 mμ) filter and 2 cm cell. A suitable size of a separatory funnel was used for the extraction.

Reagents: Standard arsenic solution; 0.6601 g of As_2O_3 (analytical grade, for standardization) accurately weighed, was dissolved in a small amount of 2N sodium hydroxide, the volume was brought to about 50 ml with water, and the acid concentration of the solution was adjusted to about 0.6N with 6N sulfuric acid. A small amount of 1N potassium permanganate solution was added and oxidized by heating. Manganese dioxide was decomposed with hydrogen peroxide, the solution was boiled, cooled, and brought to 1 *l*. Each ml of this solution contained 0.5 mg of As. This was diluted accurately to 10 volumes so that each ml of the solution contained 0.05 mg of arsenic. Phosphorus solution; $Na_2HPO_4 \cdot 12H_2O$ was dissolved in water to make a solution 1 ml of which contained about 0.03 g of P. Sulfuric acid; 3N. Sodium Hydroxide; 3N. Ammonium molybdate solution; 1 per cent aqueous solution. Hydrazine sulfate solution; 1 per cent aqueous solution. Organic solvents; Amyl alcohol, butyl alcohol, amyl acetate and butyl acetate.

(ii) Experimental method

Arsenic and phosphorus solutions were added to sulfuric acid solution and the total volume was brought to 50 ml. 7 ml of 1 per cent ammonium molybdate solution was added to this, warmed slightly to promote reaction and then cooled. This solution was placed in a separatory funnel, an organic solvent was added and extracted by shaking. The aqueous layer was then separated, the acid concentration of the solution was adjusted to 0.3~0.4N with sulfuric acid in 100 ml of total volume. 10 ml of 1 per cent hydrazine sulfate was added to this solution, the total volume was brought to 100 ml and warmed for about 10 minutes to intensify the coloration. After cooling, the absorbance of the solution was determined under the same conditions as described in the 2nd report of this series[1].

(iii) Selection of the organic solvent

Extraction was carried out on the molybdate of arsenic and phosphorus with various organic solvents and the results obtained are shown in Table 1.

Table 1

Organic solvent	Extraction	
	As	P
Amyl alcohol	Not extracted	Extracted
Amyl alcohol + amyl acetate	Not extracted	Extracted
Amyl acetate	Not extracted	Not extracted
Butyl alcohol	Not extracted	Extracted
Butyl acetate	Not extracted	Extracted

As shown in the table, neither arsenic nor phosphorus was extracted with amyl acetate, while only phosphorus, but not arsenic, was extracted with other solvents.

Amyl alcohol was chosen, because the extraction of phosphorus could be made in the best efficiency from the rapidity of the separation into two layers and other factors.

(iv) Concentration of the acid for extraction

Sulfuric acid is generally used for the coloration of molybdenum blue, so the extraction was also made in sulfuric acid solution. Concentration of sulfuric acid in the solution for extraction was varied, 0.078 mg of phosphorus was added, without the addition of arsenic and after extraction the aqueous layer was reduced and colored as described above. Results of absorbance measurements are shown in Table 2.

Table 2

Concentration of H_2SO_4 (N)	Absorbance	
0	0.622	0.620
0.1	0.070	0.071
0.2	0.068	0.070
0.3	0.069	0.068
0.4	0.070	0.067
0.45	0.080	0.082
0.5	0.100	0.100
0.6	0.125	0.127
0.7	0.261	0.263
0.8	0.374	0.370
1.0	0.590	0.588

(Blank 0.068)

As indicated in Table 2, the extraction of phosphorus molybdate alone with amyl alcohol was complete at 0.1~0.4N concentration of sulfuric acid, i. e. absorbance of the aqueous layer agreed with the experimental value of the blank test. Extraction was carried out twice with 5 ml of amyl alcohol.

Then the same experiments were carried out under the same conditions with 0.15 mg of arsenic, without the addition of phosphorus, and the results obtained are shown in Table 3.

Table 3

Concentration of H_2SO_4 (N)	Absorbance		Mean value of arsenic obtained (mg)
0.2	0.510	0.512	0.150
0.3	0.510	0.511	0.150
0.4	0.511	0.512.	0.151

(Blank 0.061)

As shown in Table 3, arsenic was not extracted at 0.2~0.4N sulfuric acid. Coloration of molybdenum blue with 0.150 mg of arsenic, without the extraction procedures under the same conditions, gave the same absorbance values of 0.510 and 0.511.

(v) Effect of the variation of phosphorus

Under the same conditions as above, varying the amount of phosphorus, without the addition of arsenic the effect of the amount of phosphorus on extraction was examined.

Table 4 (H_2SO_4 0.2N)

Amount of P (mg)	Absorbance	
0.026	0.060	0.061
0.078	0.061	0.062
0.104	0.062	0.064
0.130	0.062	0.063
0.260	0.063	0.065

(Blank 0.061)

As shown in Table 4, extraction was quite good as long as there was not a large amount of phosphorus. In the presence of a large amount of phosphorus, the amount of ammonium molybdate described above was not enough, so the extraction

was insufficient.

(vi) Separation of arsenic and phosphorus

Under the same conditions as above, extraction was carried out in the presence of both arsenic and phosphorus, and the results are shown in Table 5.

Table 5 (H_2SO_4 0.2N)

As added (mg)	P added (mg)	Absorbance		Mean value of arsenic obtained (mg)
0.050	0.078	0.225	0.226	0.051
0.100	0.078	0.360	0.358	0.100
0.150	0.104	0.521	0.520	0.152
0.200	0.104	0.652	0.651	0.201
0.250	0.078	0.800	0.803	0.250

(Blank 0.068)

As shown in the table, the determination of arsenic after separation of phosphorus gave values that practically agreed with the calibration curve obtained by the direct coloration with addition of the known amount of arsenic, without extraction procedures, as described later.

The same experiments were then carried out with the addition of iron and the results obtained are shown in Table 6, from which it may be seen that satisfactory results were obtained even in the presence of iron.

Table 6 (H_2SO_4 0.3N)

As added (mg)	P added (mg)	Fe added (mg)	Absorbance		Mean value of arsenic obtained (mg)
0.200	0.104	25	0.645	0.643	0.199
0.200	0.104	50	0.643	0.641	0.199
0.150	0.078	30	0.528	0.525	0.153

(Blank 0.068)

2. Determination of arsenic in iron and steel

A solution of 0.1~0.5 g of a sample dissolved in 10~30 ml of nitric acid (1 : 1) by heating, was boiled to remove nitrogen oxide. Arsenic and phosphorus in this solution were oxidized by the dropwise addition of 2 per cent potassium permanganate solution until persistent pink color appeared. After the solution was cooled, it was transferred to a 250-ml measuring flask, water was added up to the 250 ml mark, and 25 ml of this solution was taken and neutralized with 3N sodium hydroxide solution. About 4 ml of 3N sulfuric acid solution was added to this solution so that the total volume of 50 ml might become to be about 0.2~0.3N concentration. Then 7~8 ml of 1 per cent ammonium molybdate solution was added to this and the total volume was brought to about 50 ml and warmed slightly to accelerate the reaction. After cooling, the solution was transferred to a separatory funnel, 5 ml of amyl alcohol was added, and extracted by shaking vigorously for

about 1 minute. The funnel was allowed to stand for some time to effect perfect separation into two layers. The lower aqueous layer was then separated. When the amyl alcohol layer showed a yellow color, the aqueous layer was again extracted with another 5 ml of amyl alcohol in a separatory funnel. When the amount of phosphorus was small and the first amyl alcohol layer was colorless, sufficed it to performe one extraction. The aqueous layer was then transferred to an Erlenmeyer flask, 3N sulfuric acid was added to make the concentration 0.4N in 100 ml volume, and 10 ml of 1 per cent hydrazine sulfate solution was added, the whole volume being brought to 100 ml. After heating in a boiling water bath for about 10 minutes to intensify the coloration, the solution was cooled, transferred to the 2 cm cell, and the absorbance was measured with the Pulrich's photometer with an incandescent lamp and with S_{72} filter. The amount of arsenic was calculated from the previously prepared calibration curve.

(i) Preparation of the calibration curve

Using the standard arsenic solution, various amounts of arsenic was diluted with water, 10 ml of 3N sulfuric acid, 7 ml of 1 per cent ammonium molybdate solution and 10 ml of 1 per cent hydrazine sulfate solution were added, and the whole volume was brought to 100 ml with water. After coloration of the solution by heating in a boiling water bath for about 10 minutes, the absorbance of this solution was measured as in the case of the samples, and the relation between the amount of arsenic and the absorbance was plotted on a graph, as shown in Fig. 1.

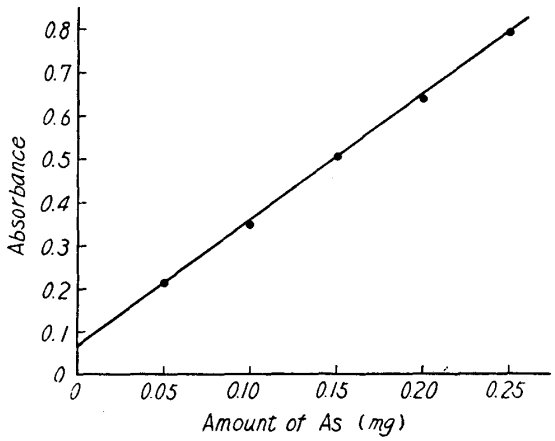

Fig. 1

(ii) Analytical results

Analytical results of the determination of arsenic in various samples by the above method are shown in Table 7, from which it will be seen that there is a tendency of slightly higher values than the values obtained by iodometry after reduction with stannous chloride. However, the results obtained gave almost constant values.

(iii) Time required for analysis

If the present method is carried out with care, the results obtained will be almost similar to those obtained by iodometry after reduction with stannous chloride. The procedures are, however, extremely simple, being not affected by the presence of phosphorus, and accordingly, it may be utilized as the rapid analytical method. The time required for rapid analysis is shown in Table 8, which indicated that quantitative determination of arsenic can be made in a simple manner, without the interference of phosphorus, within 20~30 minutes.

Table 7

Sample	$SnCl_2$-iodometry As(%)	Sample taken (g)	Absorbance	As obtained (mg)	As (%)	As mean (%)	Error (%)
Steel A	0.129	0.5000	0.278 0.280 0.280	0.070 0.072 0.072	0.140 0.144 0.144	0.142	+0.013
Steel B	0.098	0.5000	0.220 0.224 0.223	0.050 0.052 0.052	0.100 0.104 0.104	0.102	+0.004
Steel C	0.45	0.3000	0.472 0.475 0.473	0.137 0.139 0.137	0.457 0.463 0.457	0.459	+0.009
Steel D	0.49	0.3000	0.502 0.504 0.500	0.148 0.149 0.147	0.493 0.496 0.490	0.493	+0.003
Steel E	0.52	0.3000	0.532 0.540 0.530	0.158 0.161 0.157	0.527 0.533 0.523	0.528	+0.008
Steel F	0.155	0.5000	0.316 0.314 0.316	0.083 0.080 0.083	0.166 0.160 0.166	0.164	+0.009
Steel G	0.149	0.5000	0.290 0.288 0.295	0.075 0.074 0.077	0.150 0.148 0.154	0.151	+0.002
Steel H	0.110	0.5000	0.233 0.230 0.235	0.056 0.054 0.057	0.112 0.108 0.114	0.112	+0.002
Steel I	0.074	0.5000	0.187 0.188 0.186	0.038 0.038 0.037	0.076 0.076 0.074	0.075	+0.001

Table 8

Procedures	Time required (min)
Sample taken	1
Disolving	1～2
Boiling, oxydation	1
Taking an aliquot	1～2
Neutralizing, additions of reagents	2
Warming, cooling, transfering to separatoly funnel	2～3
Extraction, separation	5～7
Addition of reagent	1
Coloration	3～7
Cooling	1～2
Photometry, calculation	2
Total	20～30

Summary

(1) In the determination of arsenic as to be molybdenum blue, the same coloration occurred with phosphorus, so the quantitative determination of arsenic after isolation of phosphorus was examined. It was found that phosphorus molybdate was extracted with organic solvents, while the arsenic salt was not extracted.

(2) Amyl alcohol, a mixture of amyl alcohol and amyl acetate, butyl alcohol and butyl acetate could extract phosphorus molybdate alone but not arsenic. Neither phosphorus nor arsenic was extracted with amyl acetate.

(3) Extraction of phosphorus molybdate was perfect with amyl alcohol in 0.1~0.4N of sulfuric acid.

(4) This separation method was utilized and analytical procedures for the determination of arsenic in iron and steel samples, in the presence of phosphorus, were devised.

(5) Analytical results and the time required were shown for the determination of arsenic in several samples of iron and steel.